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THERMOELECTRICALLY-COOLED QUARTZ CRYSTAL MICROBALANCE*

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ABSTRACT

A quartz crystal microbalance is of limited value in monitoring surface contamination on satellites or in space simulation chambers because it operates several degrees above ambient temperatures. The amount of contamination adsorbed on a surface is highly temperature dependent and the higher temperature of the microbalance will significantly reduce the amount of contamination it adsorbs. Generally, a quartz crystal microbalance will indicate a lower level of contamination than the amount that is actually present. To overcome this problem, a thermoelectrically-cooled quartz crystal microbalance has been developed to monitor surface contamination as a function of temperature.

INTRODUCTION

The use of a quartz crystal microbalance (QCM) is a well established method for weighing thin films of solid materials, down to a fraction of an Angstrom, that are deposited[1] or removed[2] from a surface. Solid films couple strongly into the oscillating QCM and its frequency change is proportional to the mass loading. Direct application of a QCM to monitor a wide range of contamination in space simulation chambers has proven to be a more difficult task because a QCM operates several degrees above ambient temperatures. Gaseous contamination in equilibrium with solid materials in the chamber is not readily adsorbed on a QCM because of its higher temperatures. Contradictory results are often obtained where a passive optical system shows contamination while a QCM operating nearby indicates little is present.

As the study of surface contamination becomes more funda-

mental in nature, a QCM specifically designed to monitor contamination is needed. Not only must the heat generated by the QCM be removed, but a convenient method found to automatically control its operating temperature, so that, surface contamination studies can be made over temperature extremes common to spacecraft. To permit in-situ reflectivity measurements, the crystals should be optically polished. With these objectives in mind, a thermoelectrically-cooled quartz crystal microbalance has been developed for monitoring contamination on optical surfaces as a function of temperature.

QCM LIMITATIONS

A QCM is an active quartz crystal oscillator and power dissipation raises its temperature several degrees above the ambient. Because the amount of contamination adsorbed on a surface is highly temperature dependent, a passive surface at ambient temperature will adsorb a number of contamination monolayers until it reaches an equilibrium with sources in the chamber while a QCM will adsorb a smaller number because of the different equilibrium condition. In some cases, a heavily driven QCM will operate about 10°C above ambient. At this elevated temperature no measureable amount of contamination will be observed.

The amount of contamination adsorbed on a surface is dependent on the residence time, τ, of the contamination molecules[3].

$$\tau = \tau_o \exp(\Delta E / RT)$$

where τ_o is the vibrational period of the contamination lattice, ΔE the desorption activation energy, R the gas constant and T the absolute temperature. Griffith[4] has shown that the desorption rate of contamination with desorption activation energies of less than 25,000 cal/g mol (oil and epoxies) is highly dependent on temperature. A 10°C temperature rise can result in nearly a ten fold increase in the desorption rate. Use of a QCM to monitor contamination will consistently give lower readings than the actual level present because of its higher temperature.

The strong effect of temperature on the adsorption and desorption of contamination is shown in Fig. 1. Here long-term OGO-6 measurements are shown correlating QCM contamination loading to the eclipse period of the satellite. As has been previously reported, the primary source of contamination on the satellite was the solar panels baking out in the sun[5].

OGO-6 was inserted into a polar orbit with its orbit plane normal to the earth-sun line. This orbit was chosen so that the satellite would be in full sunlight for the maximum period after launch. During the four week period after launch, the amount of contamination adsorbed onto the QCM steadily increased until the first week in July when it abruptly decreased and finally in August the QCM showed a net loss of contamination and became a contamination source. By correlating the eclipse periods of the satellite to the QCM measurements, the reason for the fluctuation in the contamination adsorption and desorption rates became apparent.

In full sunlight the temperature of the solar panels was 72°C and a wide range of high and low volatile contamination outgassed from the panels onto the QCM. During maximum eclipse, when OGO-6 was in the earth shadow 30% of the time, the average temperature of the solar panels dropped to 60°C and the contamination flux from the panels decreased significantly. The QCM lost contamination during the eclipse period because the lower flux rate from the panels did not balance out contamination desorbing from the QCM. The QCM desorbed contamination into space and onto adjacent surfaces that were at a lower temperature than the QCM.

Although the QCM indicated a loss of contamination during eclipse, contamination was present. Reber's Neutral Mass Spectrometer, located next to the QCM, showed that a strong flux of contamination continued to outgas from the panels.

THERMOELECTRICALLY-COOLED QCM

In order to conduct contamination experiments as a function of temperature, a new instrument called a thermoelectrically-cooled QCM (TQCM) was developed. A thermoelectric device was picked to control temperature because it offers several advantages over other methods. It uses only a series of solid-state bismuth telluride junctions, through which electrical current is passed, to pump heat to or from a load by the Peltier effect. It is small in size and can be remotely operated with a signal pair of electrical leads. It has no moving parts and is highly reliable. There are no requirements for pumping a refrigerant or for supplying a coolant, such as, liquid nitrogen. These features result in greatly reduced operating and maintenance costs in controlling the temperature of a QCM with a thermoelectric device.

The design of the TQCM has been previously reported[6] and only its operation will be described here. The TQCM instru-

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mentation operating under ambient conditions is shown in Fig. 2. The TQCM Controller operates on 115 Vac, 60 Hz at 0.25 A and provides the various voltage outputs to operate the crystal oscillators, temperature bridge, thermoelectric device and readouts of temperature and frequency.

The TQCM Electronics, Heat Sink, and Sensor are shown in Fig. 3. The TQCM uses a two-stage thermoelectric device to automatically control the sensor crystal temperature between −50°C and +100°C to ± 1°C in vacuum. For operation over this range, the heat sink temperature is to be maintained below +40°C. No problem will be encountered in maintaining the heat sink below +40°C by mounting it on a 0.6 cm thick metal bracket. Heat generated by the TQCM is readily dissipated by the bracket at ambient room temperatures.

The TQCM has been designed with an extended temperature bridge circuit and reserve power and will reach a lower temperature limit of −59°C if its heat sink is maintained below +25°C. To maintain a +25°C temperature, the heat sink is to be mounted on a 1.2 cm thick metal bracket capable of removing a maximum 2.8 W when the TQCM is at −59°C. The TQCM cooldown time in vacuum is shown in Fig. 4.

The TQCM operating temperature is set by positioning the thumb wheel switch on the Controller. A 3 1/2 digit panel meter is provided in the Controller for direct readout of temperature.

A temperature output is provided for remote readout or recording. The TQCM temperature sensor is a precision platinum resistance thermometer linear to 0.5%. At 100°C the voltage output is 1.00 Vdc. At −59°C the voltage output is − 0.59 Vdc. The TQCM operating temperature in °C equals 100 times the voltage output of the Controller.

A matched pair of precision 10-MHz quartz crystals is used to measure mass loading. The crystals are designated as a sensor and reference crystal. The crystals are optically-polished and plated with Al. The sensor crystal is coated with magnesium fluoride for in-situ reflectivity measurements while contamination is collecting on its surface. The crystals can be changed by unloosening two set screws in the TQCM Sensor.

The output frequency of the TQCM is the beat frequency between the two oscillating crystals. The beat frequency effectively eliminates frequency changes caused by ambient temperature variations. By carefully matching sets of crystals in vacuum, frequency change with temperature of less than ±50 Hz between −59°C and +100°C is attained. Because only the sensor crystal sees the contamination flux, the TQCM output frequency will increase with mass loading. The crystal sensor is optically pol-

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ished and full plated on one side. This technique produces a more active crystal whose mass sensitivity is greater by about 20% than semi-polished crystals. The TQCM mass sensitivity, m, is

$$m = 3.5 \times 10^{-9} \text{ g/cm}^2\text{Hz}$$

A frequency output is provided in the TQCM Controller to measure the frequency change of the crystal sensor produced by mass loading. Frequency is measured by a counter, such as, a Hewlett Packard Model HP5321B.

The TQCM can be set at any particular temperature over its operating range. If the TQCM is set at ambient, the heat generated in the oscillating crystal will be removed so that contamination loading to passive optical systems can be monitored. By increasing temperature to about +100°C the crystal can be cleaned. By periodically dropping the temperature of the TQCM in fixed steps, the amount of surface contamination for different equilibrium temperatures can be determined and the background level of contamination in a space simulation chamber monitored with time.

The TQCM can be used to generate a calibrated contamination flux so that the contamination sticking coefficients of surfaces can be measured. A TQCM calibrated source is generated as follows. Contamination from an uncalibrated source is directed at a TQCM cooled to −50°C. Contamination is allowed to freeze out on the TQCM. The uncalibrated source is then turned off and the vacuum system allowed to pump down. The TQCM now becomes the calibrated source by simply raising its temperature so that the contamination will desorb at the desired rate. By monitoring the TQCM frequency increase with time, the contamination mass flow rate can be accurately determined.

The TQCM can also be used to calibrate the mass loading of viscous films on the quartz crystal sensor that do not couple well into the oscillating mass of the crystal. As a contamination film grows to several hundred monolayers, its top layers will slip relative to the oscillating crystal. The simple relationship between mass loading and frequency change will not hold true. Calibration is achieved by dropping the sensor temperature to freeze the contamination and provide rigid mass coupling to the crystal.

CONTAMINATION MEASUREMENTS

Studies of background contamination in a vacuum chamber

were made to show the capability of the TQCM to measure surface contamination under equilibrium conditions. A 150 l/sec Vac-Ion pump was used to evacuate the chamber to the 10^{-9} Torr range. Just prior to the measurements, the chamber was contaminated with Welsh Duo-Seal roughing pump oil that raised its pressure into the 10^{-7} Torr range.

The net mass gain or loss for an aluminum surface from the adsorption and desorption of background contamination present in the chamber at 7×10^{-7} Torr is shown in Fig. 5. Below $-30°C$ adsorption predominated and contamination collected on the surface. Above $-30°C$ desorption predominated. The break in the curve at about $-10°C$ where the rate of desorption increased abruptly is significant.

The break shows a phase change occuring in the contamination from a solid to a liquid. The phase change caused a large increase in its vapor pressure and the higher desorption rate. We were unable to make a measurement at $+20°C$ because the desorption rate became so large that by the time the surface reached $+20°C$ the contamination was nearly completely desorbed.

Fig. 6 shows the desorption rate of roughing pump oil as a function of the number of monolayers on the surface for a contamination background pressure of 4×10^{-7} Torr. When the number of contamination layers reaches 200, the increase in the desorption rate starts to level off indicating the bulk properties of the oil predominate and the properties of the surface have little effect on the desorption. At $0°C$ the leveling off of the desorption rate is quite evident.

The desorption rate decreases rapidly as the number of layers present is reduced because of the higher bonding energy holding contamination layers near to the surface. The higher bonding energy results from contamination molecules filling cracks and crevices in the polycrystalline aluminum surface.

The number of monolayers of contamination on a surface in equilibrium with the contamination on the walls of the vacuum chamber as a function of temperature is shown in Fig. 7. The ambient temperature of the chamber was $23°C$. The measurements were made by raising the TQCM temperature to $+80°C$ to bake off surface contamination and then dropping its temperature to $-50°C$ to adsorb a film of contamination. The TQCM temperature was then increased to a particular equilibrium temperature shown in the figure to determine the number of contamination monolayers. From the figure it can be seen that there was always oil contamination on the surface even at 4×10^{-7} Torr for temperatures below $+30°C$. It would have been impossible to make the measurements with a QCM because there are no net

mass changes at equilibrium.

CONCLUSIONS

Most contamination is adsorbed on a surface in the gaseous or liquid state and the adsorption rate is highly temperature dependent. A QCM is of limited value in monitoring contamination because it operates several degrees above ambient temperatures and does not readily adsorb contamination. For accurate measurements, a temperature controlled QCM should be used.

If a QCM is used to monitor contamination, measurements should be made from a directed source. The source temperature should be much higher than the QCM operating temperature to insure that the contamination sticking coefficient is greater than zero.

REFERENCES

1. Sauerbrey, G., "Application of Quartz Resonators for Weighing Thin Films and for Microweighing", Zeitschrift fur Physik, 155 206-222 (1959).

2. McKeown, D., "New Method for Measuring Sputtering in the Region Near Threshold", General Dynamics Convair Report ERR-AN-001, San Diego, Calif. (1959).

3. Vacuum Technology and Space Simulation, NASA SP-105, National Aeronautics and Space Administration, Washington, D.C.

4. Griffith, J.S., "Some Tests for Increase in Friction of Mechanisms of the Mariner Mars 1969 Spacecraft in the JPL Molsink Space Simulation Chamber", Proceedings of 4th Space Simulation Conference, AIAA/ASTM/IES, Los Angeles, Calif. (1969).

5. McKeown, D. and W.E. Corbin, Jr., "Space Measurements of the Contamination of Surfaces by OGO-6 Outgassing and Their Cleaning by Sputtering and Desorption", Space Simulation, NBS Special Publication 336, pp 113-127 (1970).

6. "Thermoelectrically-Cooled Quartz Crystal Microbalance", Operational Data, Faraday Laboratories Report FAR-73-101, La Jolla, Calif. (1973).
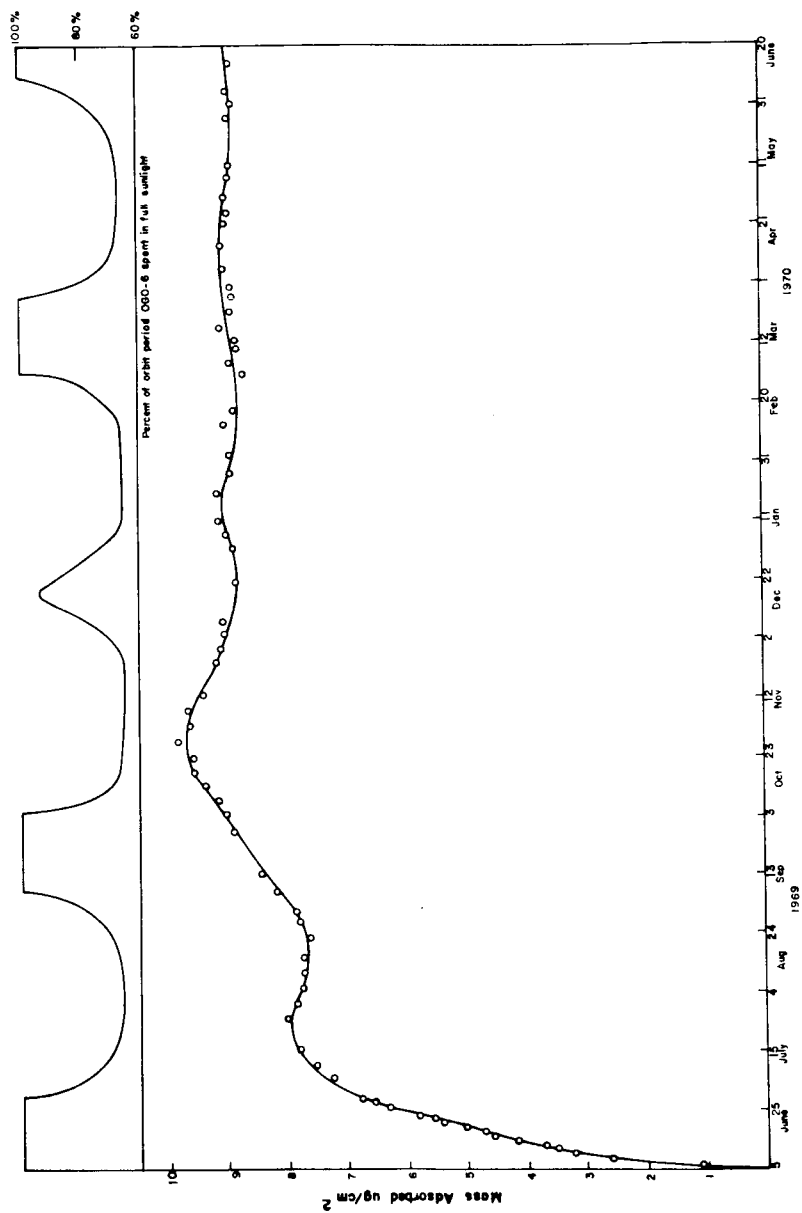
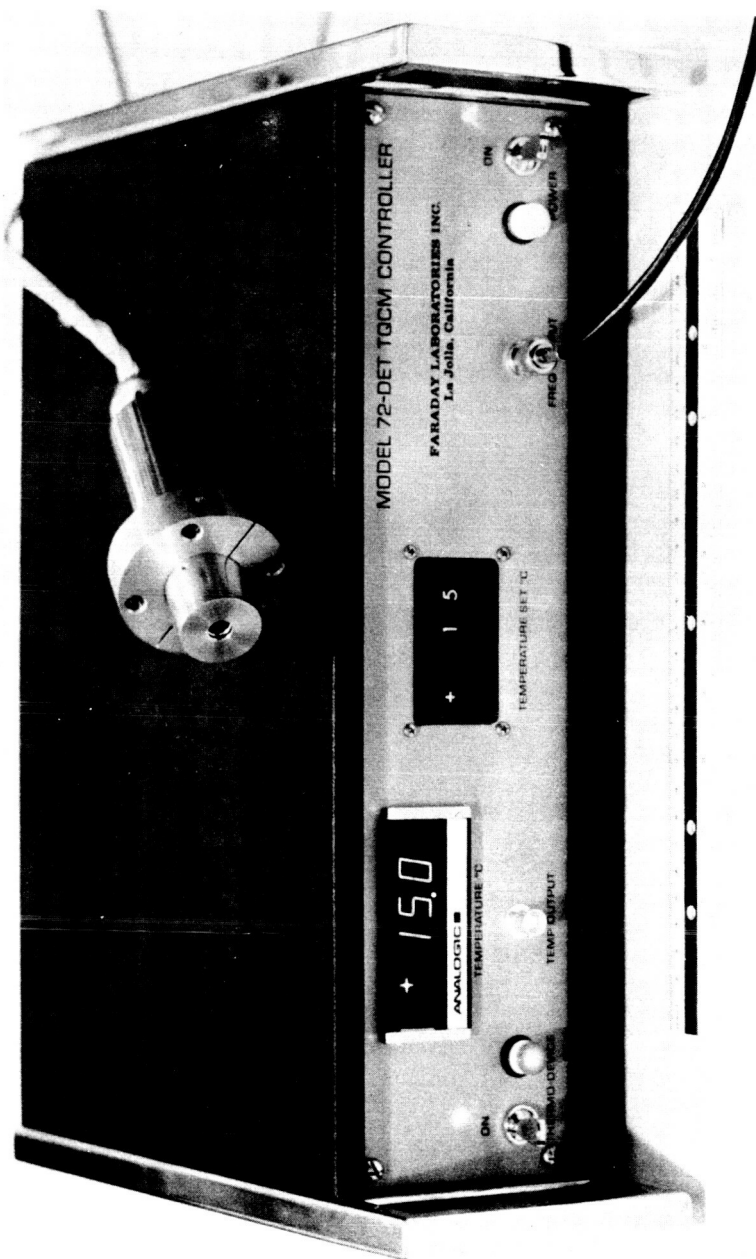Fig. 1 Long-term OGO-6 surface contamination measurements correlated to the eclipse periods of the satellite

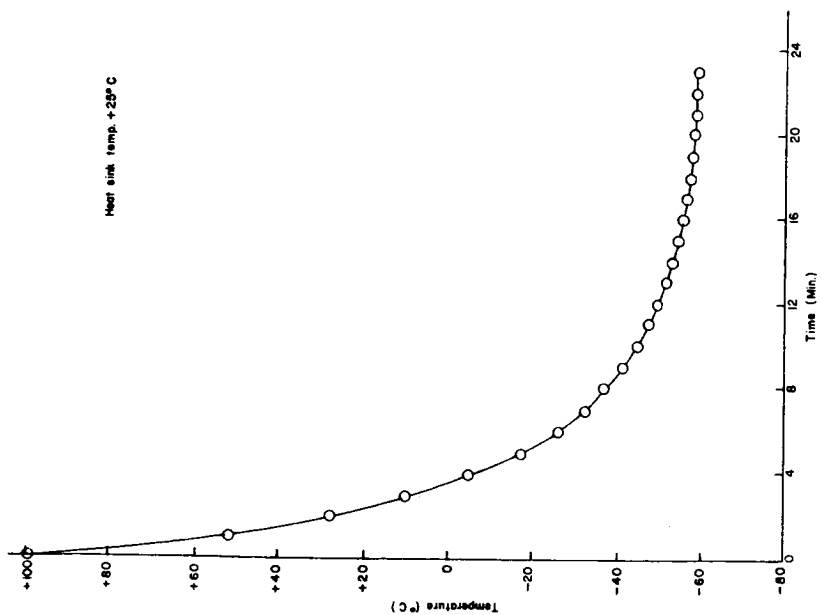Fig. 2   TQCM Operating at +15°C under Ambient Conditions

Sensor

Heat sink

Removable optically-polished
quartz crystals (1.27 cm dia)

Two-stage thermo-
electric device

Electronics

Enlarged view of sensor

Fig. 3 TQCM Electronics, Heat Sink and Sensor

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Rate $(10^{-10} g/cm^2 sec)$

Surface temp (°C)

Measurements initiated at -56°C after the surface adsorbed 2.2×10^{-6} g/cm^2 of contamination from impurities present in the vacuum system

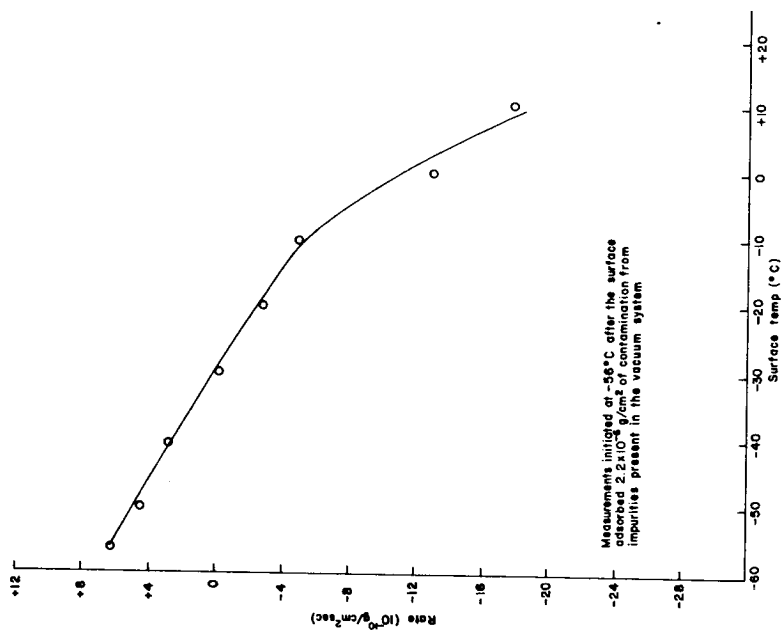Fig.5 Contamination adsorption and desorption rates for an Al surface with temperature in a 7×10^{-7} Torr vacuum
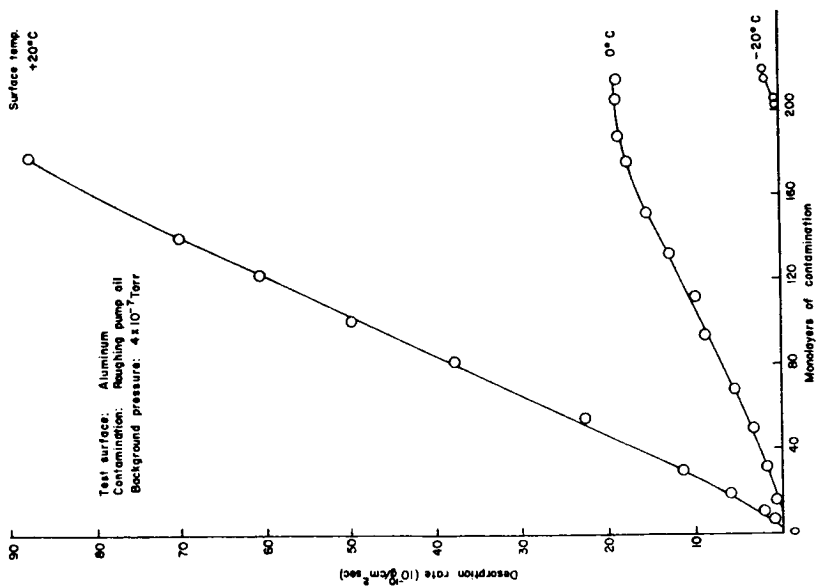

Heat sink temp. +25°C

Temperature (°C)

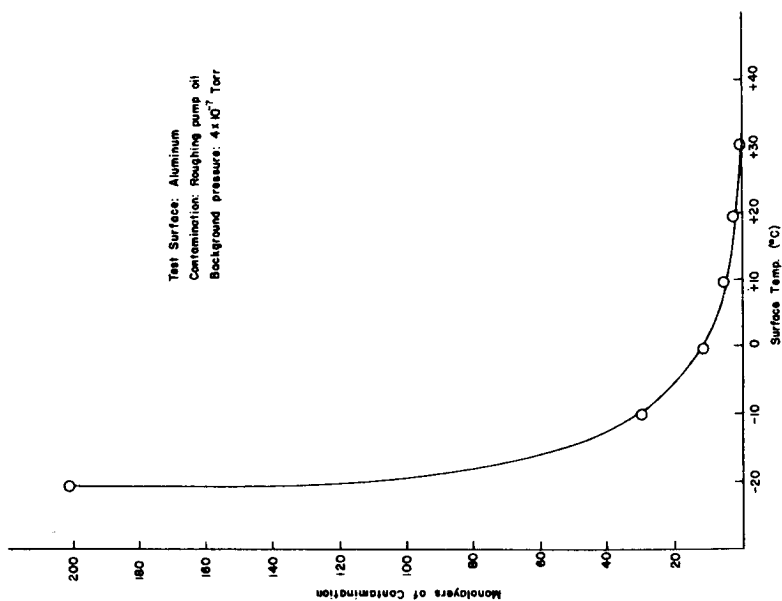Time (Min.)

Fig. 4 TQCM cool-down time in vacuum from +100°C to -59°C

Fig. 7 Number of contamination monolayers on a surface at equilibrium

Test Surface: Aluminum
Contamination: Roughing pump oil
Background pressure: 4×10^{-7} Torr

Fig.6 Contamination desorption rate as a function of monolayers on the surface

Test surface: Aluminum
Contamination: Roughing pump oil
Background pressure: 4×10^{-7} Torr

Surface temp. +20°C